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Copper(II) Complexes of Deprotonated 2-Alkylaminopyridine N-oxides and 2-Aminopicoline N-oxides

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Molecular Cu(II) complexes of deprotonated 2-aminopyridine N-oxides have been prepared by adding sodium hydroxide to aqueous slurries of their $Cu(HL)_4(ClO_4)_2$ *salts. The latter green solids were isolated from ethanolic solution with HL representative of 2-aminopyridine N-oxide (HA); 2-amino-4-, -5- and -6-picoline N-oxide, 4MAH, 5MAH and 6MAH, respectively; and 2-methyl-, 2-ethyl-, 2-propyl- and 2-isopropylaminopyridine N-oxide, MH, EH, PH and IPH, respectively. The solids are characterized by their partial elemental analyses, infrared spectra, solid reflectance and solution* ($CHCl_3$) *electronic spectra, and esr spectra of both solid and solution. The majority are isolated as anhydrous solids of various shades of tan and their spectroscopic characterization indicates them to be square planar with significant covalent character in their bonding.*

Introduction

Some time ago it was reported, [1] and confirmed recently, [2] that 2-aminopyridine N-oxide acted as a monodentate ligand by coordinating *via* the N-oxide oxygen in metal ion complexes. However, loss of one of the protons led to bidentate formation with O, N coordination with metal complexes of Fe(III) and Cu(II) [1]. We have shown that the Cu(II) complexes of the various 2-alkylaminopyridine N-oxides also bond solely *via* the N-oxide oxygen, [3] while the 2-dialkylaminopyridine N-oxides studied to date have involved O,N-chelation [4]. In addition, the 2-aminopicoline N-oxide complexes prepared and characterized in this laboratory have been found to be coordinated via only the N-oxide oxygen [5]. Therefore, amine coordination in these N-oxides apparently does not occur when either one or two hydrogens are bound to the 2-amino nitrogen.

We report here the preparation and spectral characterization of molecular Cu(II) complexes involving deprotonated amino groups attached to the heterocyclic N-oxide ring in the 2-position. The various ligands studied and their symbols used in this report are the following: 2-aminopyridine N-oxide (AH), 2-methyl-, 2-ethyl-, 2-propyl- and 2-isopropylaminopyridine N-oxide (MH, EH, PH and IPH, respectively) and 2-amino-4-picoline, -5-picoline and -6-picoline N-oxide (4MAH, 5MAH and 6MAH, respectively). Molecular complexes have recently received increased attention because of potential medicinal value due to their solubility in lipids [6].

Experimental

The green complexes $[Cu(HL)_4](ClO_4)_2$, were prepared as reported previously [2, 3, 5]. The molecular complexes were then prepared by dropwise addition of 0.1 *N* NaOH to aqueous slurries of the various $[Cu(HL)_4](ClO_4)_2$ salts past the amount when no green solid was visible. The new solids were filtered, washed excessively with deionized water and dried by pumping in a vacuum desiccator over calcium sulfate. The remainder of the experimental details as well as the instrumentation used was identical to previous studies from this laboratory [2–5].

Results and Discussion

In Table I the colors, decomposition temperatures, and partial elemental analyses are compiled. The solids are soluble in nonpolar solvents such as chloroform and ether, but sparingly soluble in polar solvents such as water and alcohols. Finally, it should be noted that attempts to preform the anionic ligands prior to introduction of the Cu(II) ion have proven unsuccessful. Therefore, the increased acidity of the amine protons on com-

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TABLE I. Colors, Decomposition Points and Partial Elemental Analyses of the Cu(II) Complexes of Some Deprotonated 2-Aminopyridine N-oxides.

Compound	Color	Decomposition Point (°C)	% Calcd		% Found	
			C	H	C	H
CuM_2	olive-tan	224	46.52	4.55	46.68	4.57
CuE_2	tan	198	49.77	5.37	49.59	5.26
CuP_2	tan	147	52.52	6.06	51.82	6.14
$Cu(IP)_2 \cdot H_2O$	olive-tan	147	50.05	6.30	50.64	5.89
CuA_2	olive-tan	190	42.63	3.58	43.13	3.62
$Cu(4MA)_2(H_2O)_2$	olive-tan	275	41.68	5.24	41.90	4.40
$Cu(5MA)_2$	pale olive	182	46.52	4.55	47.17	4.31
$Cu(6MA)_2$	olive	225	46.52	4.55	45.51	4.60

TABLE II. Partial Infrared Assignments (cm^{-1}) of Copper(II) Complexes of some Deprotonated 2-Aminopyridine N-oxides.

Compound	ν_{O-H}	ν_{N-H}	δ_{OH}	δ_{NH}	ν_{NO}	δ_{NO}	ν_{Cu-O}	ν_{Cu-N}
CuM_2					1191 s	865 m	440 m	356 s
CuE_2					1189 vs	865 s	407 s	356 s
CuP_2					1181 vs	849 m	381 s	350 s
$Cu(IP)_2 \cdot H_2O$	3570 w,b				1190 vs	845 m	413 s	338 s
CuA_2		3315 s		1625 vs	1190 vs	834 m	420 s	346 vs
$Cu(4MA)_2(H_2O)_2$	3370 m	3408 m	1655 vs	1636 vs	1178 vs	862 m	425 s	434 vs
$Cu(5MA)_2$		3355 m		1640 vs	1182 m	846 s	425 m	329 s
$Cu(6MA)_2$		3425 m		1628 vs	1180 vs	823 m	403 m	342 m

plexation of the N-oxide function is important in the formation of these anionic ligands.

In Table II we show the infrared assignments for the ligand functional groups most useful for the establishment of its bonding to the Cu(II) centers. The ν_{OH} band for $Cu(4MA)_2(H_2O)_2$ is sharp and found in a range usually associated with coordinated water [7] rather than the broad, continuous bands expected for lattice or hydrate water [8]. A DSC experiment does not show a separate band suggesting the loss of the two moles of water at its rather high decomposition temperature. Additionally, this solid possesses a band which is assignable to δ_{OH} in the 1640–1660 cm^{-1} region while the other compounds of this series show no significant absorption in their spectra. Further, bands present in the spectra of the above solid at *ca.* 830, 760 and 550 cm^{-1} are assignable to deformation modes of coordinated water [7]. Assignment of the ν_{CuO} for coordinated H_2O for $Cu(4MA)_2(H_2O)_2$ is 312 cm^{-1} [9]. The water molecule in $Cu(IP)_2(H_2O)$ is of the lattice type since it has a very broad, weak band at considerably higher energy than $Cu(4MA)_2(H_2O)_2$ and the deformation bands are absent in its spectrum.

Coordination of the N-oxide oxygen of pyridine N-oxides is usually indicated by a shift of the band assigned to ν_{NO} to lower frequency by 20–50 cm^{-1} [10] in the spectra of the complexes. In the spectra of the 2-alkylaminopyridine N-oxides and 2-aminopicoline N-oxides the intermolecular hydrogen bonding [11] lowers this band to about 1200 cm^{-1} [3, 5] (ν_{NO} for 6 MAH is 1198 cm^{-1} which has not been reported previously) and therefore, the shift in ν_{NO} for these ligands is often less. The δ_{NO} found at about 850 cm^{-1} is generally unshifted upon complexation of the neutral ligands and this lack of shifting also occurs for these anionic ligands. $Cu(6MA)_2$ has the lowest energy band assigned to δ_{NO} and the steric factor of the methyl group in the 6-position must cause this substance to have a somewhat weaker Cu–O bond.

Inspection of the ν_{CuO} band assignments in Table II shows a decrease in energy with increased size of the alkyl substituent on the amine or with increased steric hindrance in the 6-position. It should be noted that the ν_{CuO} bands in this series of ligands are some 10–20 cm^{-1} higher in energy than their analogous neutral ligands in complexes of the type $Cu(HL)_4^{2+}$ and are at the upper portion of the

TABLE III. Solid Reflectance and Solution ($CHCl_3$) Absorption Bands (kK) of Molecular Copper(II) Complexes of some Substituted 2-Aminopyridine N-oxides.

Compound	Solid	Solution ($CHCl_3$)
CuM_2	17.86, 13.04	27.10, 18.52, 13.44
CuE_2	18.52, 13.30	27.25, 18.25, 13.55
CuP_2	18.21, 13.30	27.40, 26.32sh, 18.02, 13.07
$Cu(IP)_2(H_2O)$	17.24, 12.02	27.32, 26.11 sh, 17.01, 11.49
CuA_2	17.86, 13.12	27.78sh, 17.70, 13.19
$Cu(4MA)_2(H_2O)_2$	17.76, 12.82	(27.93 sh), 17.39, 13.25
$Cu(5MA)_2$	18.12, 13.19	27.32sh, 17.54, 13.04
$Cu(6MA)_2$	17.73, 13.12	28.41sh, 17.67, 13.61

376–421 cm^{-1} range proposed for $\nu_{CuO}(PyO)$ [12].

Coordination of the amine function is indicated in the complexes by the appearance of a band in the 350 cm^{-1} region of the spectrum which is consistent with assignment of ν_{CuN}, [13]. In addition, some of the complexes have a band between 490 and 550 cm^{-1} (not included in Table II) which likely possesses some ν_{CuN} character. The complexes of 2-aminopicoline N-oxides, as well as 2-aminopyridine N-oxide, retain one hydrogen atom on their amine function and the ν_{NH} and δ_{NH} modes appear as single bands of medium and strong intensity, respectively. Of interest is that the ν_{NH} band is found at considerably higher energy than is usually associated with a coordinated amine group [14]. The reason is that this amide function is a negatively charged, electron-rich group and coordination has considerably less effect on ν_{NH} than for the corresponding neutral amines.

Compiled in Table III are the electronic spectral results obtained from solid reflectance and solution absorption measurements. There is little difference in the energies of the bands in the two spectral measurements for an individual compound indicating no change in the nature of the Cu(II) centers on dissolution. The solution spectral bands are somewhat sharper and allow assignment of a higher energy transition appearing as a shoulder (27–28.8 kK).

The band is most likely due to a O(p) → Cu(d) charge transfer. This same assignment has been made for numerous other 2-substituted pyridine N-oxide complexes [15]. In addition, most of the spectra of the compounds in this study have a second shoulder at *ca.* 29 kK on an intense intraligand band. The intraligand band which is either $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$, is relatively unshifted from its position in the spectra of the ligands. This second shoulder may also be due to this same charge transfer from oxygen, or possibly, nitrogen. A N(p) → Cu(d) charge transfer band is rarely seen at energies this low [16] because the majority of coordinated nitrogen atoms do not have a second non-bonding pair of electrons. However, one such example is a deprotonated amide group nitrogen which has been studied extensively by M. Nonoyama *et al.* [17]. Unfortunately, no mention is made of a charge transfer band involving this coordinated nitrogen.

The visible portion of the spectra features two nearly equally intense bands at *ca.* 17.5 and 12.5 kK for all the compounds with an occasional shoulder visible on one of these bands. Landers and Phillips have just recently reported a similar two peak diffuse reflectance spectrum for CuA_2 that was prepared using copper(II) acetate in boiling ethanol [2b]. Generally, Cu(II) spectra of this nature are assigned to *cis*-octahedral complexes [18] although stereochemical assignments based solely on electronic spectra should be avoided [19]. There is not a third band at lower energy in any of the spectra which might be expected for D_{2d} symmetry [20]. While 6-coordinate *cis*-octahedral stereochemistry is possible with bridging *via* either oxygen or nitrogen a square planar geometry is more likely and will be considered later in this report.

In Table IV the Esr results of the solid powders and chloroform solutions are compiled. In the powders a number of the spectra are isotropic indicating a significant interaction between Cu(II) centers [21]. Further, there is little change in the g-values in the powders when the sample is cooled from room to liquid nitrogen temperature. For the four powders having axial spectra, which are either the ones having the largest alkyl substituents on the amine nitrogen or having methyl substitutents in the 4- or 6-position, three have the typical Cu(II) spectra assigned to a $d_{x^2-y^2}$ ground state. The values for $g_\parallel$ in each of the three are somewhat lower than is usually found for CuO_2N_2 chromophores and suggests strong planar bonding and only weak axial bonding, if any. The $Cu(IP)_2 \cdot H_2O$ solid has a reversed spectrum at both room and liquid temperature but a normal

TABLE IV. Powder and Solution ($CHCl_3$) ESR Spectra of some Molecular Cu(II) Complexes Derived from 2-Aminopyridine N-oxides.

Powder Spectra

	RT			77 K		
Compound	$g_\parallel$	$g_\perp$	g_{av} or g_{iso}	$g_\parallel$	$g_\perp$	g_{av} or g_{iso}
CuM_2			2.102			2.107
CuE_2			2.084			2.086
CuP_2	2.190	2.052	2.098	2.190	2.052	2.098
$Cu(IP)_2 \cdot H_2O$	2.052	2.128	2.103	2.048	2.127	2.101
CuA_2			2.100			2.101
$Cu(4MA)_2(H_2O)_2$	2.187	2.057	2.100	2.185	2.056	2.099
$Cu(5MA)_2$			2.103			2.104
$Cu(6MA)_2$	2.221	2.050	2.107	2.223	2.052	2.109

Solution ($CHCl_3$) Spectra

	RT		77 K			
	g_o	A_o(G)	$g_\parallel$	$g_\perp$	g_{av}	$A_\parallel$(G)
CuM_2	2.103	62.3	2.199	2.043	2.095	165
CuE_2	2.102	63	2.191	2.047	2.095	173
CuP_2	2.101	63	2.193	2.044	2.094	169
$Cu(IP)_2 \cdot H_2O$	2.109	61	2.213	2.048	2.103	143
CuA_2	2.105	58	2.183	2.054	2.097	170
$Cu(4MA)_2(H_2O)_2$	2.107	61	2.187	2.054	2.098	166
$Cu(5MA)_2$	2.107	56	2.211	2.045	2.100	155
$Cu(6MA)_2$	2.106	57	2.196	2.044	2.094	163

spectrum in frozen $CHCl_3$. Other examples of this behavior have been reported [22].

In solution the A_o values are somewhat lower than what one might expect for a CuO_2N_2 chromophore but the g_o values essentially unchanged from the g-values of the solid room temperature spectra of the same compounds. In agreement with the electronic spectra this suggests that there is little change in the copper(II) sites upon dissolution. Just as the A_o values are lower than one would expect given the g_o values, so are the $A_\parallel$ values when considering both the $g_\parallel$ and the g_{av} values of the frozen solution. Note that the G values [23] for these compounds in the solid state are in the 3 to 5 range indicating weak exchange coupling between Cu(II) centers. Therefore, while the g-values are indicative of strong planar bonding for the Cu(II) centers, the various A-values are not consistent with this strong bonding when compared to related CuO_2N_2 chromophores (*e.g.*, $g_\parallel = 2.191$, but $A_\parallel = 206$ G) [24].

There is no detectable nitrogen superhyperfine splitting in the room temperature solution spectra of any of the complexes. However, each of the frozen solutions has features assignable to nitrogen coupling with varying degrees of resolution. For example, the spectrum of CuM_2 clearly shows 5 lines of approximate 1:2:3:2:1 intensity ratio on the +3/2 parallel feature which is consistent with the coordination of two nitrogens. The A(N) value is 14 G.

While the esr results in the solid suggest that there is some interaction between copper(II) centers, the solution spectra show the complexes to be 4-coordinate. Rendell and Thompson [25] have studied planar CuN_4 systems and indicate that their electronic spectra show two d–d bands, and that the greatest separation of the bands is achieved for the most planar complexes. In addition, one of us has reported [26] on a series of bis(N-alkyl-2-picolinamine N-oxide)copper(II) salts in which separation of two d–d bands by nearly 5 kK occurred when the counterion was the large tetraphenylborate anion. These Cu(II) centers showed separations of only 3–3.5 kK when the anions were either ClO_4^- or BF_4^-. Not only is there greater separation of the d–d bands but also there is a substantial increase in the energy for the tetraphenylborate salts, which is indicative of stronger in-plane bonding. Therefore, these compounds can be expected to be essentially square planar. This is consistent with the separation

TABLE V. Orbital Reduction and Covalency Parameters for some Molecular Cu(II) Complexes.

Compound	$k_{\parallel}$	$k_{\perp}$	2
CuM_2	0.632	0.677	0.726
CuE_2	0.622	0.704	0.740
CuP_2	0.614	0.676	0.730
$Cu(IP)_2 \cdot H_2O$	0.605	0.688	0.682
CuA_2	0.600	0.746	0.724
$Cu(4MA)_2(H_2O)_2$	0.608	0.739	0.718
$Cu(5MA)_2$	0.641	0.675	0.712
$Cu(6MA)_2$	0.628	0.693	0.716

of the two d–d bands, the low values of $g_{\parallel}$, g_{iso} and g_{av} in the solid state and the similarity of the g_{av} values in solid and solution spectra.

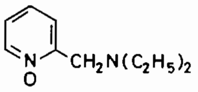
The relatively low values of A_o and $A_{\parallel}$ in the solution spectra of these eight compounds are probably indicative of substantial π-bonding involving the extra pair of electrons on nitrogen as well as the heterocyclic ring. In Table V we show the values of $k_{\parallel}$ and $k_{\perp}$, the orbital reduction factors, calculated using the equations based on Figgis [27] as follows:

$$g_{\parallel} = 2.002 + \frac{8k_{\parallel}^2\lambda_o}{E(d_{x^2-y^2} - d_{xy})}$$

and

$$g_{\perp} = 2.002 + \frac{2k_{\perp}^2/\lambda_o}{E(d_{x^2-y^2} - d_{xz;yz})}$$

In these calculations $g_{\perp}$ was obtained from $g_o = (2g_{\perp} + g_{\parallel})/3$ using the solution data, $\lambda_o = 0.828$ kK and the higher and lower energy d–d transitions were assigned as $E(d_{x^2-y^2} - d_{xz,yz})$ and $E(d_{x^2-y^2} - d_{xy})$, respectively. Since pure σ-bonding would yield a value of about 0.77 for $k_{\parallel}$ and $k_{\perp}$ [28], considerable π bonding is occurring and this π-bonding is more in-plane than out-of-plane since $k_{\parallel} < k_{\perp}$. In addition, we have calculated the covalency parameter α^2 from $\alpha^2 = A_{\parallel}/0.036 + (g_{\parallel} - 2.002) + 3/7 (g_{\perp} - 2.002) + 0.04$ and show those values in Table V. For comparison we have also calculated $\alpha^2 = 0.798$ for another square planar CuO_2N_2 chromophore, $Cu(DEA)_2(BPh_4)_2$ where DEA =



[26]. Therefore, these present compounds have considerably greater covalency and the extra pair of electrons on the coordinated nitrogens is undoubtedly responsible. The lower A values for these compounds are a result of this additional covalency.

In conclusion, we expect the eight substances included in Table V to have an essentially square planar stereochemistry with the two ligands in a *trans* arrangement. A preliminary report [29] of a single crystal X-ray study of $Cu(E)_2$ is supportive of this suggestion.

References

1 H. Sigel and H. Brintzinger, *Helv. Chim. Acta, 46,* 701 (1963).

2 D. X. West, *J. Inorg. Nucl. Chem., 43,* 3169 (1981); A. E. Landers and D. J. Phillips, *Inorg. Chim. Acta, 74,* 43 (1983).

3 W-H. Wang and D. X. West, *J. Inorg. Nucl. Chem., 41,* 1719 (1979); *42,* 1656 (1980);
K. Duffield and D. X. West, *J. Inorg. Nucl. Chem., 43,* 1517 (1981);
J. Sedgwick and D. X. West, *J. Inorg. Nucl. Chem., 43,* 2307 (1981).

4 W-H. Wang and D. X. West, *J. Inorg. Nucl. Chem., 42,* 985 (1980); *43,* 1511 (1981).

5 D. X. West, *Inorg. Chim. Acta, 71,* 251 (1983); *Polyhedron,* in press;
D. X. West and C. Nipp, unpublished results.

6 J. R. J. Sorenson, *J. Med. Chem., 19,* 135 (1976);
S. W. C. Leuthauser, L. W. Oberley, T. D. Oberley, J. R. J. Sorenson and K. Ramakrishna, *J. Natl. Cancer Inst., 66,* 1077 (1981) and references therein.

7 N. M. Karayannis, C. M. Mikulski, S. D. Sonsins, E. E. Bradshaw and L. L. Pytlewski, *Inorg. Chim. Acta, 14,* 195 (1975);
M. Teotia, J. N. Gurthu and V. B. Rama, *J. Inorg. Nucl. Chem., 42,* 821 (1980).

8 L. S. Gelfand, L. L. Pytlewski, D. L. Cosgrove, C. M. Mikulski, A. N. Speca and N. M. Karayannis, *Inorg. Chim. Acta, 32,* 59 (1979).

9 G. DeVoto, M. Massacesi, G. Ponticelli and C. Preti, *J. Inorg. Nucl. Chem., 39,* 271 (1977);
J. G. Vos and W. L. Groenveld, *Trans. Met. Chem., 4,* 137 (1979).

10 S. Kida, J. V. Quagliano, J. A. Walmsley and S. Y. Tyree, *Spectrochim. Acta, 19,* 189 (1963).

11 M. C. R. Symons and D. X. West, unpublished results.

12 T. P. E. Auf der Heyde, C. S. Green, D. E. Needham, D. A. Thornton and G. M. Watkins, *J. Mol. Struct., 70,* 121 (1981).

13 S. S. Parmer, *Ind. J. Chem., 15A,* 459 (1977).

14 M. Biddau, M. Massacesi, R. Pinna and G. Ponticelli, *Trans. Met. Chem., 3,* 153 (1978).

15 L. S. Gelfand, L. L. Pytlewski, C. M. Mikulski, A. N. Speca and N. M. Karayannis, *Trans. Met. Chem., 4,* 354 (1979);
D. X. West and R. J. Hartley, *J. Inorg. Nucl. Chem., 42,* 711 (1980);
D. X. West and W-H. Wang, *J. Inorg. Nucl. Chem., 42,* 985 (1980) and references therein.

16 S. Bunel, C. Ibarra, M. Rodriquez, A. Urbina and C. A. Bunton, *J. Inorg. Nucl. Chem., 43,* 971 (1981).

17 M. Nonoyama, *Inorg. Chim. Acta, 13,* 5 (1975) and references therein.

18 B. J. Hathaway and D. E. Billing, *Coord. Chem. Rev., 5,* 143 (1970).

19 S. E. Linvingstone and J.E. Oluka, *Trans. Met. Chem.*, *2*, 190 (1977).

20 R. M. Gaura, P. Stein, D. X. West and R. D. Willett, *Inorg. Chim. Acta*, *60*, 213 (1982) and references therein.

21 Y. Nakao, W. Mori, T. Sakura and A. Nakahara, *Inorg. Chim. Acta*, *55*, 103 (1981).

22 M. N.Chary and B. A. Sastry, *Ind. J. Chem.*, *16A*, 521 (1978).

23 B. J. Hathaway, *J. Chem. Soc., Dalton Trans.*, 1196 (1972).

24 G. D. Shields, S. Christiano and R. D. Bereman, *J. Inorg. Nucl. Chem.*, *40*, 1953 (1978).

25 J. C. T. Rendell and L. K. Thompson, *Can. J. Chem.*, *57*, 1 (1979).

26 D. X. West and K. K. Bennett, *J. Inorg. Nucl. Chem.*, *43*, 3021 (1981).

27 B. N. Figgis, 'Introduction to Ligand Fields', Interscience, New York, 1966, p. 295.

28 R. S. Naidu and R. R. Naidu, *J. Inorg. Nucl. Chem.*, *41*, 1625 (1979).

29 P. Knuuttila and H. Knuuttila, private communication.